Development of PEM Electrolysis at Elevated Temperatures

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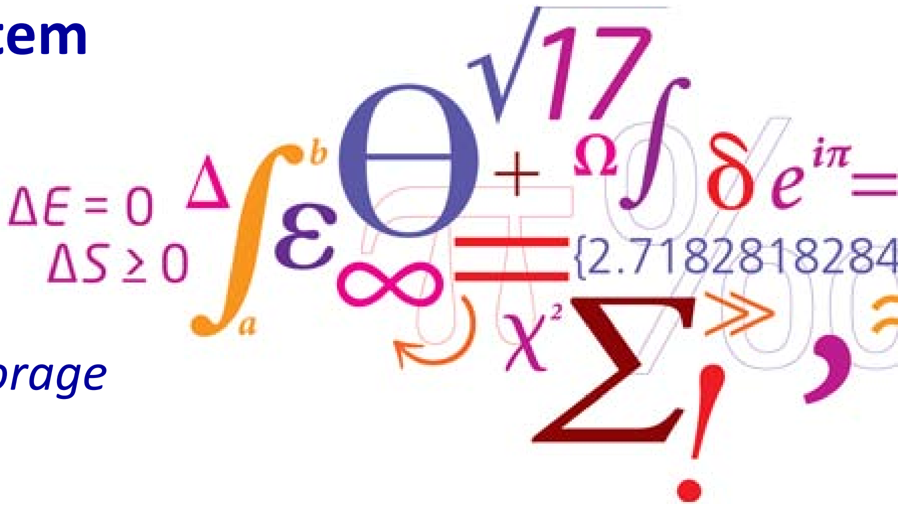
International Symposium:
Water Electrolysis and Hydrogen as part of the future Renewable Energy System
10-11 May 2012, Copenhagen



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Projects completed 2011

WELTEMP: "Water Electrolysis at Elevated Temperatures",
European Commission, FP7

HyCycle: "Center for Renewable Hydrogen Cycling",
Danish Council for Strategic Research (DSF)

Projects ongoing 2012

MEDLYS

MEDLYS: "Medium temperature Water Electrolysers",
Danish Council for Strategic Research (DSF)

PROCON: "Danish-Chinese Centre for Intermediate Temperature Proton conducting Systems",
Danish National Research Foundation (DNRF)

Concept of Research

Elevated temperature (≥120°C)
- To obtain higher efficiency (Kinetics and thermodynamics!)
(steam or liquid?)

Requires New Materials Development due to strongly increased demands to materials:

Component:	*To replace/modify:*
Membrane	Nafion
Current collectors	Titanium
Bipolar plates	Titanium
Catalysts	IrO_2, RuO_2, Pt: Are they stable?

MEAs → Electrolyser

The WELTEMP Project and the Partners
www.weltemp.eu

FP7, Collaborative Project, small or medium-scale focused research project
Duration: January 1st, 2008 - April 30th, 2011
Total costs: 3.2 million Euro EC Funding: 2.4 million Euro

The Partners

Technical University of Denmark (Coordinator)	Denmark
Institute of Chemical Technology Prague	Czech Republic
Institute of Macromolecular Chemistry ASCR	Czech Republic
The Norwegian University of Science and Technology	Norway
IHT Industrie Haute Technologie SA	Switzerland
Acta S.p.A.	Italy
Tantalum Technologies A/S	Denmark
Danish Power Systems ApS	Denmark

The partners of HyCycle
(Electrolysis and Photocatalysis, www.hycycle.dk)

Technical University of Denmark, DTU Energy Conversion (coordinator)

Center for Individual Nanoparticle Functionality (CINF), Department of Physics, Technical University of Denmark

Center for Atomic-scale Materials Design (CAMD)
Department of Physics, Technical University of Denmark

Department of Physics and Chemistry, University of Southern Denmark

Institute of Chemical Engineeing, biotechnology and Environmental Technology
University of Southern Denmark

IRD Fuel Cells A/S, Denmark

Danish Power Systems ApS, Denmark

Tantaline A/S, Denmark

Objectives

(1) Membranes:
Temperature-resistant polymer membranes, *operational temperatures ≥ 120°C*
Anion conducting (Alkaline) membranes should be surveyed as well.

(2) Electrocatalysts:
Stability of IrO_2 based anodes and Pt cathodes at temp. ≥ 120°C should be demonstrated.
Low loadings!
New non-noble metal catalysts for use under alkaline conditions.

(3) "Construction materials":
Development of current collectors and bipolar plates made in steel coated with tantalum, and having excellent corrosion-, contact resistance- , and conductive properties.

(4) Membrane Electrode Assemblies (MEAs):
Methods for preparation of membrane-electrode assemblies (MEAs) with targets of fabrication of MEAs single cell performance approaching 1.55 V at 1.0 A/cm² at a temperature above120°C

(5). Test Electrolysers:
Design, construction and testing of a prototype electrolysers

Concepts of Polymer Membrane Materials

1) PBI (polybenzimidazol)

- Phosphoric acid doped (apparently not stable!)

2) PFSA (Perfluorosulfonic acid, *Nafion, Aquivion*)

- Water is required to be present inside the structure - otherwise no proton conductivity
- Water evaporates from the membrane at T > 100°C then three ways to go:

a) Modify Nafion/Aquivion by adding hygroscopic fillers (steam or liquid water)

b) Doping with H_3PO_4! (only steam feeding)

c) Pressurising the cell and working with liquid water

3) Anion conducting membranes (alkaline ”PEM” electrolysis)

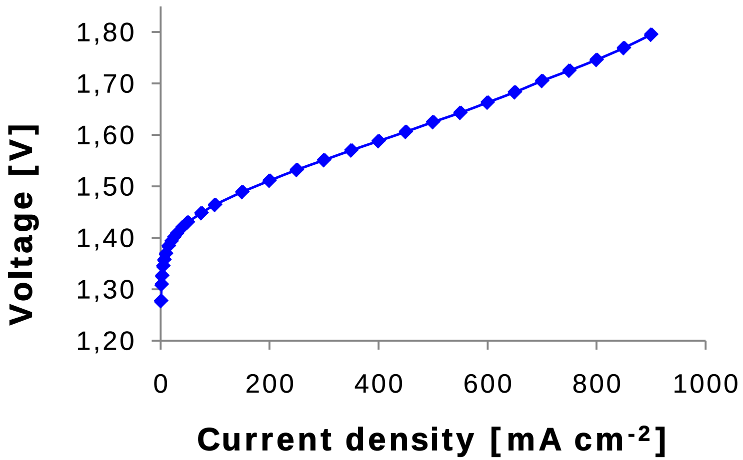
Nafion®

PBI

Aquivion™
"Short side chain"-
PFSA

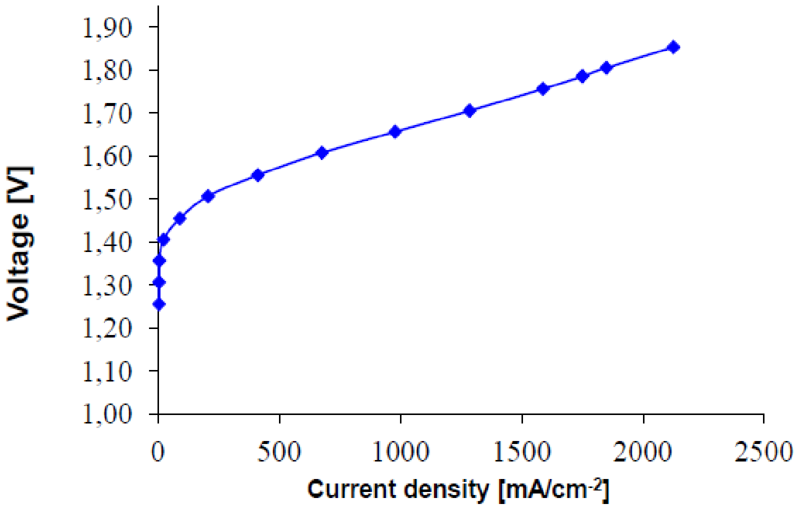
Steam- or Pressurized Water Electrolysis?

STEAM electrolysis:
PFSA Membrane (Aquivion)
doped with H_3PO_4



Anode: 0.98 mg/cm2 IrO_2, Cathode 0.34 g/cm2 Pt, GDL 0.5mm Ta coated steel felt, Aquivion membrane, 63µm thick, Temperature 130°C, Atmospheric Pressure

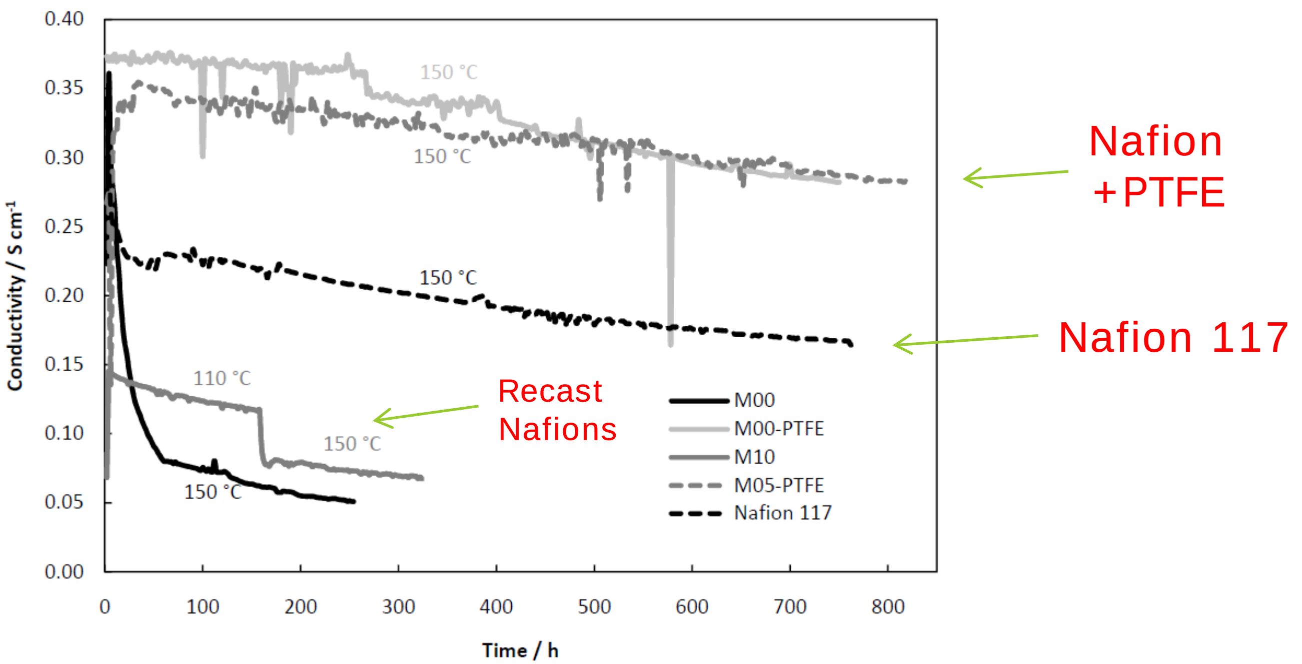
Pressurised LIQUID water electrolysis
PFSA Membrane (Aquivion)



Anode: 1.72mg/cm2 IrO_2, Cathode 0.80 g/cm2 Pt, GDL 0.5mm Ta coated steel felt, Aquivion membrane, 60 µm thick, Temperature 120°C, Pressure 3 bar

Ionic conductivities of membranes

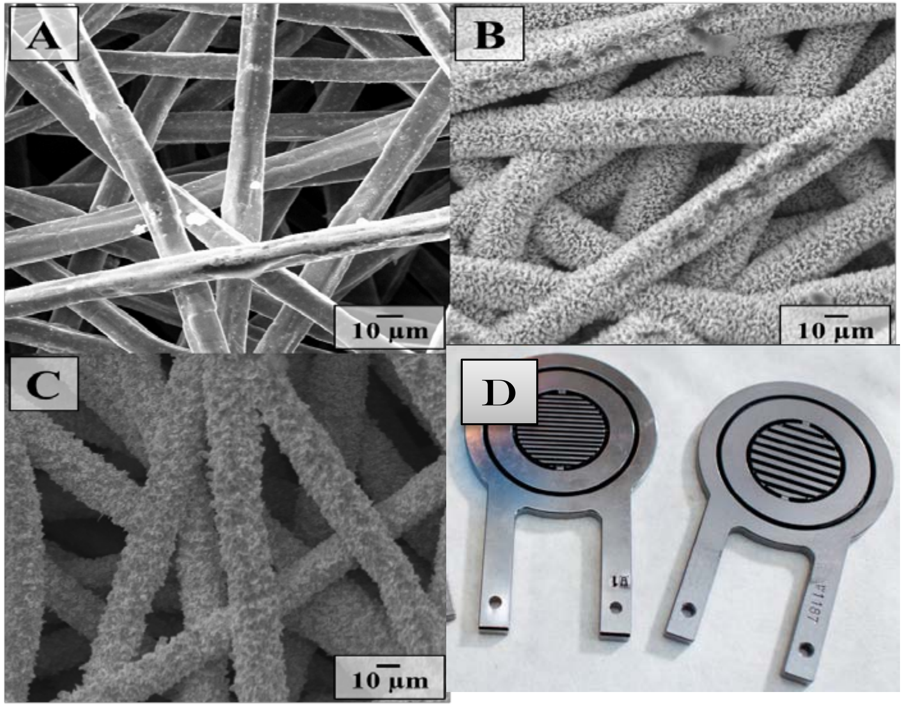
Membrane materials:
(Mechanical)Reinforcement
is important to conductivity



150ºC, 6 bar, 100 % RH

Construction materials:

Tantalum coated steel to replace titanium



A: Steel felt (uncoated)

B and C:
Tantalum coated steel felts

D: Labscale flowplates coated with tantalum

Flowplates and anodic current collectors ("GDL"):
Titanium not stable – replaced by tantalum coated steel
CVD: Chemical Vapor Deposition

$2TaCl_5\,(g) + 5H_2(g) \rightarrow 2Ta + 10HCl(g)\uparrow \quad (800^oC)$

Desired corrosion rate in 85 % H_3PO_4: $\leq$ 0.1mm/year

Corrosion rate of TITANIUM vs. temperature and the extent of polarization

v_k [mm/a]	80 °C	120 °C	150 °C
-500 mV	*43*	*498*	*2283*
E_{kor}	*31*	*451*	*2142*
750 mV	*0.2*	*437*	*2815*
2000 mV	*0.4*	*485*	*2632*
2500 mV	*0.2*	*-*	*41*

Corrosion rate of TANTALUM vs. temperature and the extent of polarization.

v_k [mm/a]	80 °C	120 °C	150 °C
-500 mV	*<0.01*	*<0.01*	*0.3*
E_{kor}	*<0.01*	*<0.01*	*<0.01*
500 mV	*<0.01*	*<0.01*	*<0.01*
2000 mV	*<0.01*	*<0.01*	*<0.01*
2500 mV	*<0.01*	*<0.01*	*<0.01*

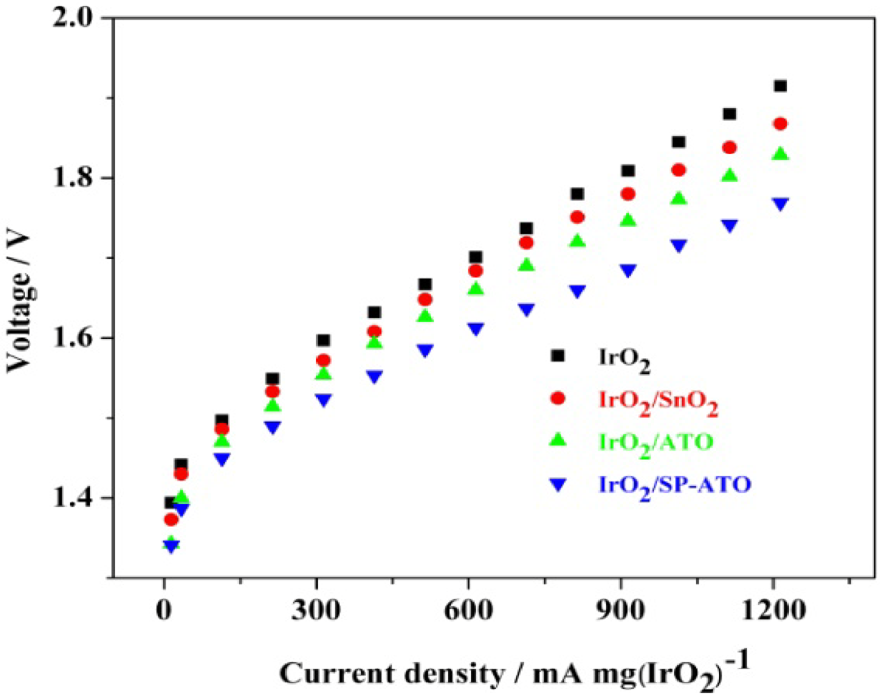
Catalyst Materials / Catalyst Support Materials:

Cathode: Pt / C

Anode: IrO_2 with
or without *support*

Supports:
SnO_2
SnO_2–Sb_2O_3 (electronic onduct.)
SnO_2–Sb_2O_3-"$SnHPO_4$"(elect.+proton!)

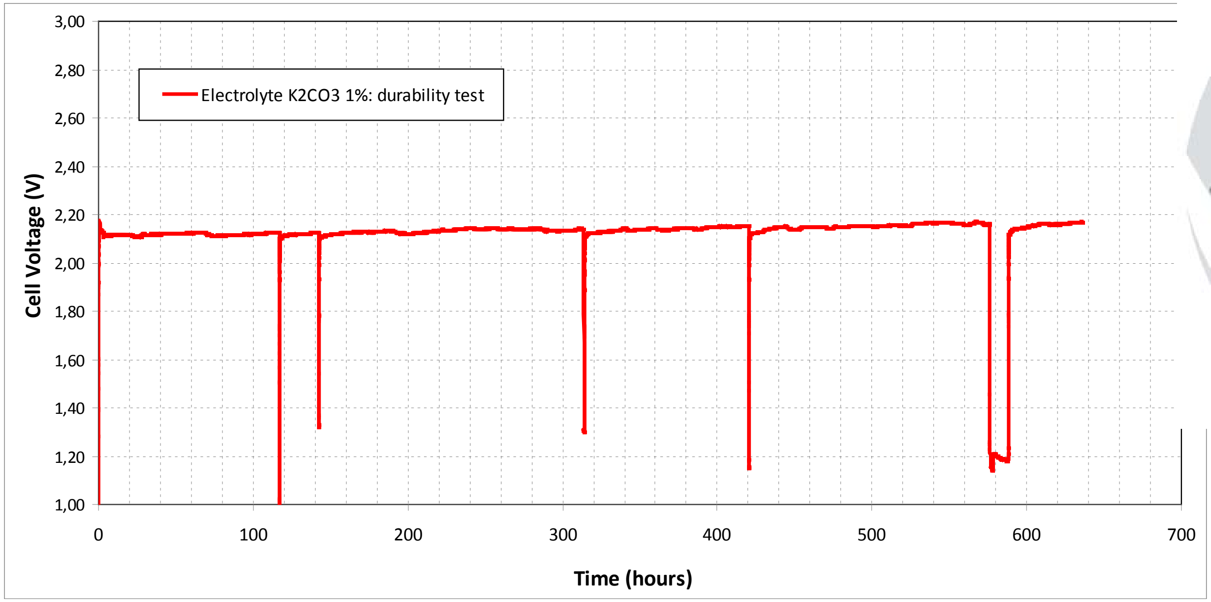
TiO_2 (non-conductive supports:
SiC - can also provide an improved
performance !)



PEM steam electrolysis at 130 °C and atmosphere pressure.
The anode loadings were 0.7 mg cm^{-2} IrO_2, 1.4 mg cm^{-2} IrO_2/SnO_2, 1.4 mg cm^{-2} IrO_2/ATO, and 1.4 mg cm^{-2} IrO_2/SnP-ATO, respectively.
The cathode was made of 40 % Pt/C at a loading of 0.7 mg Pt cm^{-2}.
Membranes used were PA doped Aquivion (0.05 mm).

Alternative concept: Alkaline MEAs

Durability issue ?



AES100 – 300 Stacks from Acta-nanotech
30 bars, no compressor
alkaline membranes

Life test obtained with the ACTA alkaline MEA 475 mA/cm^2),T_{cell} = 40 ° C.
Now more than 6000 h!

Performance problem: Main issue is ionomer for catalyst layer preparation (Teflon was used).
Active non-noble metal catalysts were developed for both anode and cathode!

Medium temperature / Intermediate temperature cell

Temperatures : 200-400^{0}C

MEDLYS and PROCON projects:

Inorganic proton conducting membranes:

CsH_2PO_4
Nb-P
Bi-P
Nd-P
etc.

Various alternative (non-noble element) catalysts will be tested.

Achievements/Breakthroughs

- PEM Steam electrolysis can be carried out
- PFSA membranes can be made conductive at high temperatures by phosphoric acid doping.
- Reinforced membranes provide higher conductivity
- Pressurised cells reached higher performances than steam electrolysers at 130^{o}C (until now...)
- Tantalum coated steel felt as anode GDL
- MEAs based on anion conductive/alkaline membranes can be prepared, high durability at temp. up to 60^{o}C have been observed.
- Alkaline MEAs, working without noble metals.

Application perspectives

The research represents a survey of various types of electrolyser technologies:

Acidic PEM, Alkaline PEM, Liquid water feeding, steam electrolysis (÷SOEC)

PEM: decentralized units *Alkaline: Centralized units*

For large scale use in the nearer future according to governmental plans, alkaline technologies will be important!

(Denmark: 50 % of total electricity consumption from sustainable sources in 2020=>
Large electricity storage capacity will be needed very soon!)

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Danish Power Systems, Denmark

Thank You for your attention!